

STRUCTURAL AND MAGNETIC PROPERTIES OF MnAs NANOCLUSTERS FORMED BY Mn ION IMPLANTATION IN GaAs

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Abstract

Ferromagnetic (FM) nanostructures embedded in semiconductors are of fundamental interest since their physical properties could be used in new devices such as memories, sensors or spintronics.

In this work, we present results obtained on the synthesis and characterization of nanosized MnAs ferromagnets buried in GaAs. These nanocrystals are formed either by single Mn implantation or Mn+As co-implantation at room temperature into GaAs wafers at 141 and 180 keV respectively. Two doses, 1×10^{16} and 2×10^{16} ions.cm⁻² for each impurity, are tested. Pieces of the wafers are then annealed by RTA or classical furnace annealing at various temperatures under N₂ atmosphere for increasing times.

HRTEM and diffraction analysis show that under such conditions MnAs precipitates form with a regular hexagonal structure, the 3m orientation-relationship of precipitates with respect to the matrix offers the most energetically stable configuration. Size distributions are systematically extracted from statistical analysis of "2 beam" TEM images. The precipitate mean diameters of nanocrystals populations range from 9 to 13 nm depending on the annealing conditions.

Magnetization measurements by SQUID magnetometry on the same samples reveal a progressive transition from a superparamagnetic behavior at room temperature to an FM one at 2K, reflecting a distribution of blocking temperature, due to distribution of size and to dipolar interactions. Curie temperatures in the range of 360K were measured.

1. Introduction

New hybrid magnetic semiconductor materials with low dimensions are of great fundamental and technological interest, as both the charge and the spin of the carriers can be used, which opens new fields in spintronics [1]. New devices such as memories, sensors, for example, may be developed by taking advantage of these new physical properties and their small size. Among the different possibilities to achieve ferromagnetic (FM) semi-conductors, the incorporation of Manganese in a GaAs substrate is one of the most promising. Most of the current studies deal with Molecular Beam Epitaxy to fabricate (Ga,Mn)As diluted phases [1]. These systems display Curie temperature (T_C) in the range of 80-110K, therefore limiting their potential application. Higher T_C can be reached by forming pure MnAs phases. Nanoclusters (ncs) can be formed also by means of MBE [2-3]. However, Mn ion implantation in GaAs followed by heat treatment is another route to synthesize nanocluster populations of MnAs embedded in a GaAs matrix [3-7]. The advantages of this method are the accurate control of the depth positioning of ncs through the energy of the ions, the density of ncs by adjusting the dose and the mean size by tuning the thermal treatment. In this work, we present a full analysis of the effects of the synthesis conditions on nanosized MnAs ferromagnets characteristics fabricated by Mn ion implantation. The Manganese profiles are followed by Secondary Ion Mass Spectrometry (SIMS) on as-implanted and annealed samples for various doses, annealing temperatures and times. We show the effect of the Mn diffusivity on the final material. The impact of co-implantation is analyzed. The crystalline structure and the magnetic properties are obtained respectively by Transmission Electron Microscopy (TEM) and SQUID magnetometry. Finally we propose two routes for a successful synthesis of this material.

2. Experimental details

In order to fabricate MnAs nanomagnets, the goal is to introduce from 2 to 4 % of Mn in the GaAs crystals which corresponds to doses in the 10^{16} ions.cm⁻² range. We have studied two different conditions of implantation in semi-insulating (001) GaAs wafers. In the first case, we performed a co-implantation of Mn and As ions at energies of 141 keV and 180 keV respectively. These energies were chosen from a TRIM calculation in order to get the same depth for both Mn and As maximum concentrations, and to keep good stoichiometry along the Mn and As concentration profiles. The calculated projected range (Rp) corresponds to 77 nm. The second case is a single Mn ion implantation at 141 keV. For both cases, two doses have been investigated : 1×10^{16} and 2×10^{16} ions.cm⁻², which correspond respectively to a supersaturation of Mn of about 2% and 4 %.

Subsequently, implanted samples were annealed in a rapid thermal annealing (RTA) system, at various temperatures ranging from 600 to 850°C for several durations from 15 to 120 seconds under a N₂ atmosphere and using a face-to-face method to avoid surface degradations. This thermal treatment induces several phenomena necessary for a proper synthesis of nanomagnets such as the solid phase epitaxy (SPE) of the GaAs matrix amorphized by ion implantation, the diffusion and nucleation to form MnAs precipitates and finally the growth of nanoclusters.

Several characterization methods have been used to study the material. The chemical composition and the distribution of Mn during annealing were investigated by Secondary Ion Mass Spectroscopy (SIMS) on an IMS 4/6F CAMECA analyzer. The structure of the nanoclusters was studied by conventional and High Resolution Transmission Electron Microscopy (TEM) on CM20 and CM30 Philips microscopes, respectively. Finally the

magnetization of the samples was measured with a Superconducting Quantum Interference Device (SQUID) MPMS-5S Quantum Design magnetometer.

3. Results and discussion

3.1 Chemical analysis.

SIMS measurements have been carried out on all samples to follow the different fabrication steps from as-implanted to annealed. Figure 1 shows the Mn concentration profiles for a single implantation of manganese at a dose of 2×10^{16} ions.cm⁻² and for a co-implantation of Mn + As, at a dose of 2×10^{16} ions.cm⁻². The RTA annealing conditions were 750°C for 1min in both cases. The as-implanted profiles (dotted line) are identical within experimental precision. In this profile, the projected range R_p is about 78 nm in good agreement with the TRIM simulations. At a depth of 150 nm, a shoulder is observed which corresponds to the crystal/amorphous interface. The profile corresponding to the single implantation exhibits a large diffusion of Mn toward the surface and into the depth of the matrix. Around R_p , a large fraction of the Manganese atoms are lost. This Manganese has either been oxidized on the surface, as has been shown by TEM where a MnO₂ phase was detected, or segregated at the End of Range (EOR) defects at roughly 150 nm below the surface where a secondary peak is present in the SIMS profile. On the contrary in the co-implanted profile it can be seen that most of the Mn remains close to the initial projected range of the as-implanted sample. In this case the loss of manganese around R_p is small. At the lower dose of 1×10^{16} ions.cm⁻² and for the same annealing conditions, for both single and co-implantation, Mn concentration profiles exhibit a large diffusion of Mn. These results suggest that in a Mn+As co-implantation process, high doses are necessary to preferentially form MnAs nanoclusters.

In figure 2 we have plotted the Mn concentration profiles for different RTA annealing temperatures ranging from 600°C to 850 °C for one minute. This graph corresponds to a co-

implantation at a dose of 1×10^{16} ions.cm⁻². It is clear that at 600°C the Manganese remains around the $R_p = 78$ nm, while for higher temperatures (650°C and 850°C) the Manganese diffuses rapidly towards the surface and the crystal/amorphous interface in a first step, and finally toward greater depth in the GaAs for high temperatures. It is noticeable in figure 3, that both Mn profiles remain the same for both rapid thermal annealing (RTA) at 600°C for 1 min or classical furnace annealing (CTA) at 600°C for 30min. From these SIMS studies we conclude that for high implantation doses, a co-implantation Mn+As is necessary to trap the manganese at its original location whatever the thermal annealing. For a lower dose, the temperature has to be reduced to 600 °C to have a significant amount of the manganese remaining around the R_p . From figure 2 and 3 it is clear that the diffusion process is activated at temperatures ranging between 600 °C and 650 °C. This could be put in relationship with the congruent temperature of GaAs ($T_G = 630^\circ\text{C}$) [8] when Arsenic begins to evaporate, which leads to a large injection of vacancies in the crystal.

3. 2 Structural properties.

The same set of samples were observed by cross-sectional TEM images and by HRTEM. Figure 4(a) shows a High Resolution TEM image of one precipitate fabricated by a co-implantation at a dose of 2×10^{16} ions.cm⁻² and annealed at 750°C for 1 min. A large precipitate with a diameter of about 9 nm is imaged. In this case, the crystal structure is hexagonal with characteristic lattice parameters $a = 0.37 \pm 0.01$ nm and $c = 0.57 \pm 0.01$ nm compatible with a MnAs composition. These values correspond to the well-known stable hexagonal phase MnAs. Most of the time, the orientation relationship between the matrix and the precipitates is $(0002)_{\text{MnAs}} // (\bar{1}\bar{1}\bar{1})_{\text{GaAs}}$ and $[\bar{1}2\bar{1}0]_{\text{MnAs}} // [011]_{\text{GaAs}}$. The observed orientation relationship (OR) is $3m$ which provides the minimum interfacial and elastic energies for the precipitate/matrix. There are four variants of this OR.

Figure 4(b) is a cross-section image obtained on a co-implanted sample at a dose of 2×10^{16} ion.cm⁻² after RTA annealing at 750°C for 1 min. In this picture, we can observe a good regrowth of the crystalline matrix and a population of nanoclusters at about 80 nm below the surface. Some extended defects, identified as End of Range (EOR) defects, are present at a depth of 150 nm which corresponds to the former crystal/amorphous interface. From a statistical analysis of the image, a mean diameter of about 12.8 nm was measured for the nanoclusters population in this case. TEM images have been taken for the single Mn implants and for lower doses with annealing temperature higher than 650°C. No nanoclusters could be observed in these cases. However, on the images obtained on samples annealed at a temperature of 600 °C, whatever the annealing time or method (RTA or CTA) used, nanoparticles were again found. These observations correspond perfectly with the SIMS profiles behavior described in the previous section. When the manganese remains at its original location either for the higher dose of the co-implanted samples or for an annealing temperature lower than 650°C nanoclusters are formed. In the other cases, the loss of manganese is too high and no clusters can be formed. If these conditions are respected, nanoclusters are formed with a broad size dispersion displaying an average diameter ranging from 9 to 13 nm, depending on the annealing conditions.

3. 3 Magnetic properties.

Magnetization measurements have been performed systematically on the different systems. Hysteresis loops have been measured at 2 and 300K, as well as the temperature dependence of the magnetization according to the zero field cooling procedures between 2 and 400K in a field of 200G. In most of the samples only the diamagnetic response of the GaAs substrate was evidenced. Interestingly only the samples containing MnAs ncs display a ferromagnetic signature. Figure 5(a) displays the extracted ferromagnetic response of the

MnAs ncs in a high dose co-implanted sample ($[\text{Mn}] = 2 \cdot 10^{16} \text{ cm}^{-2}$, $[\text{As}] = 2 \cdot 10^{16} \text{ cm}^{-2}$) annealed at 750°C for 1 min. At 2K, the magnetization curves display a hysteretic behavior typical of a FM material. At room temperature, hysteresis disappears, which is characteristic of superparamagnetism. The superparamagnetic behavior [9] is confirmed by the zero field cooled – field cooled measurements (ZFC-FC) presented in Figure 5(b). We observed a wide curve for the ZFC cycle which reflects a wide distribution of blocking temperatures T_B . This broadening of T_B is probably due to both the size distribution of ncs and to dipolar interaction fields between nanoclusters. Curie temperature (T_C) of this system was about 360 K.

The different systems of MnAs ncs display the same behaviors. The relative high T_C as compared to bulk MnAs phases ($T_C = 318\text{K}$) can be ascribed to a small amount of Ga in the ncs. GaMn phases have large T_C in the range of 600°K . Ncs of $\text{MnAs}_{1-\varepsilon}\text{Ga}_\varepsilon$ with small ε value should have lattice parameters near the MnAs since Ga and As have atomic radii in the same range, but with higher T_C , as previously observed by P.J. Wellman et al [6-7].

4. Conclusion

We have successfully formed MnAs nanosized ferromagnets in semi-insulating (001) GaAs by Mn ion implantation and subsequent annealing. The properties of such a system have been studied by SIMS, TEM and SQUID magnetometry. We have underlined the importance of the annealing process and particularly of the temperature on Mn diffusion. We have two different behaviors for temperature under and above the congruent temperature of GaAs, $T_G = 633^\circ\text{C}$. We have determined the position, the nature and size distributions of the nanoclusters by TEM. A mean diameter from 9 to 13 nm is observed. The ncs population exhibits a ferromagnetic behavior at low temperature. Superparamagnetic behavior is observed at higher temperature with a wide distribution of the blocking temperatures which reflects the size distribution of ncs size and dipolar fields. We also found a higher $T_C = 360\text{K}$

than the bulk possibly due to some Ga mixing in MnAs. This study has identified two ways to successfully synthesize MnAs nanoclusters using ion implantation.

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Figure Captions:

Fig. 1. SIMS measurement of Manganese concentration of (Mn,As):GaAs and Mn:GaAs annealed at 750°C, 1min ($[Mn] = 2.10^{16} \text{ cm}^{-2}$; $[As] = 2.10^{16} \text{ cm}^{-2}$). As-implanted profile is drawn as dotted line.

Fig. 2. SIMS measurement of Manganese concentration of (Mn,As):GaAs ($[Mn] = 1.10^{16} \text{ cm}^{-2}$; $[As] = 1.10^{16} \text{ cm}^{-2}$) annealed for 1min at various temperatures.

Fig. 3. SIMS measurement of Manganese concentration of (Mn,As):GaAs ($[\text{Mn}] = 1.10^{16} \text{ cm}^{-2}$; $[\text{As}] = 1.10^{16} \text{ cm}^{-2}$) annealed at 600°C for two different durations.

Fig. 4. (a) Cross-sectional TEM image ("2 beams", $g = (220)$) of (Mn,As):GaAs annealed at 750°C , 1min ($[\text{Mn}] = 2.10^{16} \text{ cm}^{-2}$; $[\text{As}] = 2.10^{16} \text{ cm}^{-2}$). (b) High Resolution TEM image of a single MnAs nanoparticle of (Mn,As):GaAs annealed at 750°C , 1min ($[\text{Mn}] = 2.10^{16} \text{ cm}^{-2}$; $[\text{As}] = 2.10^{16} \text{ cm}^{-2}$).

Fig. 5. Magnetization measurements of (Mn,As):GaAs annealed at 750°C , 1min ($[\text{Mn}] = 2.10^{16} \text{ cm}^{-2}$; $[\text{As}] = 2.10^{16} \text{ cm}^{-2}$). The diamagnetic response has been removed. (a) Hysteresis loops at room temperature and $T = 2\text{K}$; (b) Zero field cooled – field cooled magnetization measurement for $H = 200\text{oe}$.